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Fuel Canister Stress Corrosion Cracking Susceptibility Experimental Results

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Assistant Secretary for Environmental Management
Office of Nuclear Material and Spent Fuel

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CONTENTS

FIGURES

TABLES

ACRONYMS

ASTM	American Society of Testing and Materials
ATR	Advanced Test Reactor
DI	deionized
DOE	U.S. Department of Energy
GTAW	gas tungsten arc weld
LME	liquid metal embrittlement
MCO	mult-canister overpack
SCC	stress corrosion cracking
SNF	spent nuclear fuel
SSRT	slow strain rate test

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1. INTRODUCTION

The National Spent Nuclear Fuel Program is tasked with ensuring the U.S. Department of Energy (DOE)-owned spent nuclear fuel (SNF) is acceptable for permanent disposal at a designated repository. From a repository acceptance criteria viewpoint and from a transportation viewpoint, of significant concern is the condition of the container at the time of shipment. Because the fuel will be in temporary storage for as much as 50 years, verification that no significant degradation has occurred to the canister is required to preclude repackaging all the fuel. Many canisters are also being removed from wet storage, vacuum dried (hot or cold), and then placed into dry storage. This process could have a detrimental effect on canister integrity. Research is currently underway to provide a technically sound assessment of the expected canister condition at the end of interim storage.

Several studies have been completed to evaluate the potential interactions within the canister over time, and several more are in progress. One such study of chemical interactions on two representative fuel types indicated a potential for the presence of cesium and rubidium liquid metal.[1] In this form, a potential may exist for liquid metal embrittlement (LME). However, if any water is available, these two elements may react to form metal hydroxides. The presence of cesium or rubidium hydroxide (caustics) could cause a stress corrosion cracking (SCC) problem within the canisters. A project was initiated to evaluate the likelihood for either of these conditions to result in a compromise of canister integrity during interim storage.

A review of some published literature indicated the risk of LME was remote primarily because of the propensity for these two elements to react with any available water. Vacuum drying processes do not remove 100% of all liquid, just the bulk of any free water. Thus, bound water would be present in the storage container that could be released during fuel degradation. Little research has been performed on the SCC capability of cesium/rubidium hydroxide. However, caustic solutions similar to these hydroxides, such as sodium hydroxide, are known to cause SCC in stainless steel.[2]

In order to increase the confidence of an intact canister after interim storage, a series of experiments was performed to evaluate the SCC susceptibility of two candidate canister materials (Type 304L and 316L stainless steel) to a range of possible environmental conditions (temperature and solution composition). The susceptibility of a material to SCC can be estimated using a wide variety of test methods. These tests provide only indications of a material's susceptibility to SCC, not definitive proof. Three different types of tests were performed in an attempt to reduce the uncertainty of the results. Included are crevice, U-bend, and slow strain rate tests. Triplicate tests were also used to evaluate for reproducibility. However, the final conclusion cannot be more than a "best scientific estimate" and should not be used as an absolute value.

2. SENSITIVITY ANALYSIS SUMMARY

A number of sensitivity studies were performed to evaluate the expected integrity of SNF storage canisters after interim storage. This information will be required prior to approval for transportation and acceptance at a repository. One study estimated the potential for interactions between the fuel components with the canister material. Two fuel types were selected to represent the bulk of DOE-owned SNF. Zirconium alloy-clad uranium metal fuel, represented by N-Reactor fuel, makes up about 85% of DOE-owned SNF, based on metric tonnes of heavy metal. Uranium is known to degrade quickly when exposed to moisture, and much of the stored fuel is currently in a damaged condition. N-Reactor fuel is currently being repackaged into Type 304L multicanister overpacks (MCOs) (165 × 24-in. diameter), which hold 243 Mark IV assemblies.

Aluminum-based fuel will also be evaluated, represented by Advanced Test Reactor (ATR) fuel. Although aluminum-based fuels are a small percentage of the total DOE inventory, they are typically highly enriched with a larger burnup. Thus, the amount of fission products in this fuel group is one of the largest. Aluminum is also fairly reactive with water. ATR fuel will be stored in a standardized DOE SNF canister constructed of Type 316L stainless steel. The 10-ft, 18-in. diameter canister will hold 20 ATR assemblies. Based on the potential for degradation, these two fuels will bound most of the DOE-owned SNF (see Reference 1).

Several conditions had to be assumed prior to performing the interaction analysis. The fuel was assumed to be aged 90 years after removal from the reactor and a negligible amount of water was available. Canisters were expected to remain intact, containing all gaseous and liquid reaction products. The cladding was assumed to have failed, and all fuel components were released and available for interaction. Temperatures as high as 400°C were considered; this was a conservative estimate based on SNF being located near commercial fuel in a repository. But, more realistic temperatures were also evaluated, 20, 100, 200, and 350°C. Although the canisters will be situated horizontally in the repository, it was assumed that any tilt would result in liquid accumulating near one end. Composition of the fuel elements was estimated using ORIGEN2, and the thermodynamic calculations were performed with HSC Chemistry software (see Reference 1).

Gaseous, liquid, and solid products from complete disintegration of the SNF in a storage canister were assessed. Results indicated three potential paths for compromising the canister structural integrity after 90 years: (1) overpressurization from fission product gases, (2) hydrogen embrittlement (addressed in a subsequent report), and (3) LME. The last risk was based on the presence of the alkali metals cesium and rubidium. Fuel composition ratios dictate that a mixture would contain 60 to 90 wt% cesium, with the balance essentially rubidium. Both of these metals have low melting points (28°C for cesium and 39°C for rubidium). Thus, liquid alkali metals could be in contact with the stainless steel, a condition with the potential for LME (see Reference 1).

Further study began of the risks associated with liquid cesium and rubidium in an interim SNF storage canister. An assessment indicated that LME would not be a significant risk (discussed in the next section). However, one assumption used in the initial sensitivity study was that a negligible amount of water was available. Actual conditions may not be represented by this assumption. Most of the N-Reactor and ATR fuel are placed in water prior to dry storage. Many elements were damaged prior to storage or were degraded significantly during water storage. A drying process was used to remove the bulk water before the SNF was put into dry storage, but residual water is inevitable. It is highly likely that the cesium and rubidium will react with any available water to form oxides or hydroxides. Alkali hydroxides (in particular sodium hydroxide) have been known to cause SCC in austenitic stainless steels. Thus, a review of the potential for cesium or rubidium hydroxide mixtures to cause SCC in Type 304L and 316L alloys was included in the assessment.

3. LIQUID METAL EMBRITTLEMENT

Anderson (see Reference 1) stated that under certain conditions, liquid cesium and rubidium would be present within a canister of ATR or N-Reactor SNF during interim storage. It was assumed that 100% of the elemental composition of the fuels was available, no water was present, and temperatures ranged between 20 and 400°C. Under these conditions, about 3 moles of cesium and 1 mole of rubidium will be in the ATR canister, and 9 moles of cesium and 3 moles of rubidium will be in an MCO. The melting temperature of cesium and rubidium are 28 and 39°C, so the metals will likely be in liquid form. Liquid metal can cause embrittlement of solid metals under certain conditions, resulting in unexpected rupture of a material. Thus, an assessment of the potential for cesium and rubidium to cause LME in the canister stainless steel materials was completed.

LME is a special form of material failure where a thin layer of a liquid metal in intimate contact with a susceptible solid metal causes a transition from the ductile phase to the brittle phase. Subsequent tensile stress causes rapid brittle fracture in the material. The failure is not the result of a corrosion, dissolution, or diffusion phenomenon and does not correlate with time of exposure. LME occurs near the melting point of the liquid metal. At higher temperatures, the material begins to transition back to the ductile phase, and the risk of premature fracture is reduced. The liquid must wet the solid (be in intimate contact) for LME to occur. Small amounts of liquid metal can cause embrittlement, but postfracture surfaces have also been covered by the liquid. Fractures are usually brittle intergranular cracks with little branching, indicating a quick propagation. Generally, the liquid needs to coat the crack tip for a fast fracture.[3]

Susceptibility to LME is specific to particular metal couples. Cesium has been found to embrittle cadmium metal, but not iron or nickel (the primary components in stainless steel) (see Reference 3). Experiments with several stainless steel materials in liquid rubidium have shown that LME is not likely. C-ring tests with Type 316 and 304 stainless steels in liquid rubidium at temperatures between 400 and 672 K showed no indications of cracking. However, pitting of Type 304 was observed.[4] Tensile experiments with austenitic stainless steels (including Types 304 and 316) in liquid rubidium were compared to the same material in an argon atmosphere at 50 and 150°C. No reduction in ductility was identified and in fact appeared to increase at 50°C.[5]

Based on the information available, it is assumed that liquid cesium or rubidium will not cause LME of Types 304L and 316L stainless steels. However, both of these elements will react with any moisture to form oxides or hydroxides. A potential exists for alkali hydroxides to cause SCC in austenitic stainless steels and has been reported with sodium hydroxide. Thus, the assumption of no moisture present in the canisters is no longer conservative.

Additional literature references were investigated that examined the SCC susceptibility of stainless steels to cesium and rubidium hydroxide. SCC is generally a problem with caustic solutions above a concentration of 25% and a temperature of 100°C.[6] In experiments at the Idaho National Engineering and Environmental Laboratory, one set of wedge-opening load tests was performed with rubidium hydroxide and four alloys, including Type 316 stainless steel. No cracking was seen after 5,600 hours in 63% and 72% rubidium hydroxide at 129 and 139°C, respectively. However, the more highly alloyed Nitronic 50 did not show any indications of cracking until after 5,600 hours.[7] Because crack initiation does not begin until after an unknown induction period, it is not clear if 316L is resistant to cracking or if the test was ended prematurely. No information was found on the effects of cesium hydroxide.

Because research on the SCC susceptibility of stainless steels in cesium and rubidium hydroxide solutions is limited and the results available are questionable, laboratory experiments were planned. Below is a description of the test matrix, the resulting data, and conclusions.

4. TEST DESCRIPTION

SCC is the brittle fracture of a normally ductile material. It occurs as result of a combination of factors including a susceptible material, a corrosive environment, and the presence of tensile stresses. Corrosion of the material acts in a synergistic way with low stresses (such as residual stresses from welding) to cause crack initiation at some surface failure. Once the crack has been initiated, propagation occurs based on the condition at the crack tip. Metallurgical condition (such as grain size, secondary phases, etc.) of the material may also play a role in crack propagation. Ultimately, final fracture occurs. SCC of austenitic steels is typically associated with chloride containing solutions. However, it has also been seen with caustic solutions such as sodium hydroxide.[8]

SCC is a recognized failure mechanism for austenitic stainless steels, particularly when exposed to chloride solutions. However, cases of failure in caustic solutions (primarily sodium and potassium hydroxide) have been reported. Both transcrystalline and intercrystalline cracking have been identified. Formation of carbide precipitation has been suggested as an area of weakness susceptible to intercrystalline SCC. This occurs near welds where the temperature is optimum for carbon to react with chromium and precipitate at the grain boundaries. Welding is also a source of residual stresses. The difficulty in predicting SCC lies in the lack of visible indicators. Cracking can initiate on a microscopic scale and then quickly propagate to an unrecoverable extent. It does appear, however, that catastrophic failure in austenitic steels is not common. Rather the cracks are small enough to cause leaking in pipes, vessels, etc., without sudden large fractures. Temperature and caustic concentration do affect the resistance of the materials and are considered in the test matrix described below.[9]

Increasing the confidence of an intact canister after interim storage will be achieved by measuring the SCC resistance properties of austenitic stainless steels exposed to cesium and rubidium hydroxide. The susceptibility of a material to SCC can be estimated using a wide variety of test methods. Three were selected for this project: crevice, U-bend, and slow strain rate tests (SSRTs). Crevice tests provide information on the crack initiation; U-bend tests focus on both initiation and propagation; and SSRTs compare final fracture results. Material types and conditions (welded, surface preparation, etc.) were chosen based on proposed SNF interim storage canister materials. Solution chemistry was varied according to the expected storage conditions, and initially two temperatures were selected to estimate trends.

These tests provide only indications of a material's susceptibility to SCC, not definitive proof. Three different types of tests were performed in an attempt to reduce the uncertainty of the results. Triplicate tests were also performed to evaluate for reproducibility. However, the final conclusion cannot be more than a best scientific estimate and should not be used as an absolute value.

4.1 Test Methodology

Three test methods were selected to increase the confidence that a result would be applicable to the actual service, an SNF canister in dry storage after wet storage. Included are crevice, U-bend, and slow strain rate tests. Standard practices are available for each test method that was used; the crevice tests followed ASTM G 78-95, the U-bend tests followed ASTM G 36-94, and the slow strain rate tests followed ASTM G 129-95. Coupon preparation and evaluation was according to ASTM G1-90. Crevice tests consist of a section of the candidate material (coupon) in close contact with another sample, typically a washer of either the same material or Teflon. Teflon was used in these tests. A bolt assembly was used to maintain the configuration. Close contact between two materials forms a very small gap, called a crevice. Solution can seep into the crevice, but free mixing with the bulk solution does not occur. Thus, stagnant conditions are created, and the solution chemistry can change causing accelerated localized corrosion, typically in the form of pitting. Although these tests are not specifically designed for SCC, they do indicate the susceptibility of material to localized corrosion. In addition, pitting in a material can be an initiator to cracking.

The coupon assembly was immersed in the selected solution at a specified temperature for the test duration. Test vessels, made of Teflon with full reflux condensers, were placed in water baths to maintain a constant temperature. After 42 days, the crevice coupons were removed from solution, disassembled, and examined with a stereomicroscope at 70X for initiation of pitting or cracking. Results from crevice tests are reported as number and depth of pits identified, weight changes, and any additional changes in the visual appearance of the coupon.

A strip of material bent in the shape of a U and held in place by a bolt arrangement to induce a specific stress is called a U-bend coupon. Residual tensile stress is induced on the outer side of the coupon from the bending action. The inner side is in compression, but only the tensile stresses contribute to the increased risk of SCC. As with the crevice method, the coupon was suspended in the solution at the designated temperature. The same equipment used in the crevice tests was used for the U-bend tests. The bolts are hung from a Teflon hanger that is attached to the vessel lid. This immerses the bent portion of the coupon, but the ends are exposed to the vapor space of the vessel. As discussed earlier, SCC is a function of material stress and the environment. Increasing the stress in the material by bending the coupon results in more severe conditions and accelerates the onset of crack initiation. It may also accelerate crack propagation once the initiation has occurred. Approximately once per week, the U-bend coupons were removed and examined with a low magnification microscope (10X to 70X) for indications of cracking (without removing the bolt assembly). If no cracking was observed, the coupons were returned to the test solution. The tests continued for approximately 6 months. Any cracks or other visual changes identified on the coupon were reported in the results.

SSRTs require a tensile instrument to pull a tension specimen very slowly. Strain (units of extension divided by the gage length per time) is applied at a slow constant extension rate (units of extension per time). A strain rate is typically 10^{-4} to 10^{-8} s^{-1}; slow enough to allow the corrosive environment to act on the material but fast enough to have results in a reasonable time. For the purposes of these tests, the strain rate was 10^{-6} s^{-1}. The test ended when the coupon fractured. Similar to the U-bend test, the SSRT method increases the stress on a material resulting in an accelerated test.

A baseline or control, stress-strain curve was generated by exposing a coupon to deionized water at a designated test temperature. Subsequent tests exposed samples to the desired solution at a designated temperature while being stressed. The resulting curves are then compared to the baseline. Accelerated breaking times indicate the environment is increasing the tendency for that material to crack. No definitive values are determined in this test method. Technical judgment was required to interpret the results when comparing the stress-strain curves.

4.1.1 Test Material

Two austenitic stainless steels are currently proposed for SNF canister material. Type 304L stainless steel is the material of construction for the MCO being used at Hanford for N-Reactor fuel. Type 316L is the current material choice for the standardized canister. Therefore, both metals were included in the test project. The “L” designation indicates low carbon (less than 0.03% compared to less than 0.08% for normal grades) requirements in the material. The lower carbon content reduces the potential for sensitization. Carbon can react with the chromium in the alloy matrix at certain temperatures (between 1,100 and 1,300°F), forming a chromium carbide precipitate at the grain boundaries. The resulting chromium depletion in the matrix increases the susceptibility of the material to corrosion (known as sensitization). Areas near welding operations are exposed to the optimum temperature for sensitization for the longest time period. Increased time at the temperature increases the carbon-chromium extent of reaction and, thus, the susceptibility to corrosion. Most of the samples were welded using the gas tungsten arc weld (GTAW) process. Welds were positioned across the U-bend coupons at the point of maximum bend. Tensile samples for the SSRT were machined with two-weld configurations. One set of experiments will be performed with a weld longitudinally through the tension coupon, and one set will be performed with a weld transversely across the gage area. In addition, at least one unwelded coupon was used in each test method to evaluate the effects of welding on cracking susceptibility.

Nuclear grade 316 stainless steel (316NG), which has tighter controls on the amount of carbon, has been proposed as a canister material. Thus, the 316NG was included in the original test design (see Reference 2). Funding and schedule constraints, however, required the reduction of the number of experiments that could be performed. The 316NG tests were eliminated from the test matrix.

4.1.2 Environmental Conditions

Solution chemistry was based on the thermodynamic assessment of two representative fuel canister configurations reported in Reference 1. Under the conditions described in that document, cesium and rubidium will be present as a liquid metal. However, there was no moisture present in the theoretical system, and there will most certainly be water, entrained or free, in the actual canisters. The results from the initial assessment were extended to include the formation of cesium and rubidium hydroxide.

Concentrations were selected based on best technical judgment, assuming the conservative side of a realistic value. Initially, two solution chemistries were chosen and are shown in Table 1. Bromine and iodine, also present in the ATR and N-reactor fuel elements, readily oxidize rubidium and cesium and were, therefore, included in the solution chemistries (see Reference 1). Once the molar ratios of the relevant components in the solution were defined, dilutions to 40 and 20 wt% caustic (rubidium and cesium hydroxide) in deionized water were made. Both concentrations were used in the test matrix. A third solution without halides was added to investigate the role of the bromine and iodine. In addition, control tests were performed with deionized water.

Experiments were planned at two temperatures, 50 and 90°C. The test plan (see Reference 2) stated that the two atmospheres planned were air and helium. The latter may be used as a cover gas in some SNF storage canisters. However, funding and schedule constraints required a reduction in the original test matrix. Thus, tests at 50°C and those with helium were eliminated based on the assumption that higher temperatures and air atmosphere will be conservative and bound the lower temperature and helium atmospheric conditions. Triplicate samples were tested in the crevice and U-bend tests, but only a single sample for each configuration was used in the slow strain rate tests. Table 2 has the complete test matrix.

Table 1. Chemical composition of the test solutions.

Solution	#1 20% OH (w/ B and I)	#2 40% OH (w/ B and I)	#3 40% OH (w/o B and I)
CsOH	0.57 M	1.14 M	1.14 M
RbOH	1.12 M	2.24 M	2.24 M
NaBr	0.004 M	0.004 M	
NaI	0.015 M	0.015 M	

Table 2. Stress corrosion cracking test matrix.

Test Solutions	316L No weld	316L T weld	316L L weld	304L No weld	304L T weld	304L L weld
90°C Deionized water		Crevice U-bend SSRT	SSRT		Crevice U-bend SSRT	SSRT
90°C 20% caustic (w/ B and I)		Crevice U-bend SSRT	SSRT		Crevice U-bend SSRT	SSRT
90°C 40% caustic (w/ B and I)	U-bend	Crevice U-bend SSRT	SSRT	U-bend	Crevice U-bend SSRT	SSRT
90°C 40% caustic (w/o B and I)		Crevice U-bend			Crevice U-bend	

SSRT = Slow strain rate test

5. EXPERIMENTAL RESULTS

5.1 Type 316LW Crevice Tests

Welded Type 316L (316LW) crevice experiments at 90°C were tested for 42 days. Results, which are listed in Table 3, indicate that the general corrosion rates were extremely low. The general industry standard considers corrosion rates <2 mils per year (mpy) to be acceptable corrosion rates. Corrosion rates in the halide free solution are not significantly different than the solution with iodine and bromine, so corrosion inhibition from the halides is not indicated. No indications of pitting or cracking were seen in any of the tests. Figures 1 through 4 show the final appearance of the coupons from the test solutions. The color of the coupons tested in deionzed water (Figure 1) has remained unchanged except for an occasional oxide (rust) spot; the coupons tested in the hydroxide solutions have turned a brown color as a result of the chemical attack. Examination by scanning electron microscopy found the layer too thin for chemical analysis, estimated at only a few angstroms thick.

Table 3. Type 316LW crevice test corrosion rates at 90°C.

Coupon ID	Alloy	Solution Tested	Corrosion Rate (mpy)
07	316LW	Deionized water	(-0.002)
08	316LW	Deionized water	0.002
09	316LW	Deionized water	0.008
	(Disregard (-) rate)	**Average Rate =**	**0.005**
W4223	316LW	20% OH **(w/ B and I)**	0.02
W4224	316LW	20% OH **(w/ B and I)**	0.04
W4225	316LW	20% OH **(w/ B and I)**	0.03
		Average Rate =	**0.03**
W4275	316LW	40% OH (w/ B and I)	0.08
W4276	316LW	40% OH (w/ B and I)	0.04
W4277	316LW	40% OH (w/ B and I)	0.03
		Average Rate =	**0.05**
10	316LW	40% OH (w/o B and I)	0.07
11	316LW	40% OH (w/o B and I)	0.05
12	316LW	40% OH (w/o B and I)	0.05
		Average Rate =	**0.06**

Figure 1. Type 316LW tested in deionized water at 90°C.

Figure 2. Type 316LW tested in 20-wt% hydroxide solution with halides at 90°C.

Figure 3. Type 316LW tested in 40-wt% hydroxide solution with halides at 90°C.

Figure 4. Type 316LW tested in 40-wt% hydroxide solution without halides at 90°C.

Coupons tested in the 40-wt% hydroxide solutions (Figures 3 and 4) are darker than the ones tested in the 20-wt% hydroxide solution (Figure 2). Different photography techniques have made this color contrast less apparent in the pictures. Coupons from the 20-wt% hydroxide solution and 40-wt% hydroxide solution without halides show a tinted "footprint" where the crevice washer had been, but very little localized corrosion has occurred. Interferometry techniques detected no discernible depth to the crevice area. The surface roughness of the corrosion site appeared to be the same magnitude as the rest of the coupon. The welds are etched in all the hydroxide solutions tested. Neither the etched welds nor the minor accelerated crevice corrosion are severe enough to indicate an early failure mechanism.

5.2 Type 316LW U-Bend Tests

Type 316LW U-bend tests in the deionized water were immersed for 6 months at 90°C. None of the three test coupons have shown any clear indication of cracking. A very small weight loss trend indicated a small level of general corrosion was occurring, and this correlates to the results of the crevice tests. The coupons did not darken, but some small rusty spots were visible randomly across the surface. Figure 5 shows the post-test appearance of the coupons.

None of the 316LW U-bend test coupons had any clear indications of cracking after 6 months exposure to the three hydroxide solutions. Microscopic examination of coupon numbers 2, 5, and 6 during the first week showed an opening that appeared to be deformation damage. No changes were seen throughout the test period, and they were assumed to have occurred during the bending of the coupon. Although the primary analysis method with U-bend tests is visual, some weight measurements were made before and after exposure. Small weight losses (less than 0.1 g) indicate some general corrosion was occurring, which correlates to the results from the crevice tests. Figures 6 through 8 show the condition of the U-bend coupons in 20% and 40% cesium/rubidium/hydroxide with iodine and bromine. The hydroxide solution turned the coupons dark brown as seen in Figures 6 and 8. The general corrosion appears worse in the area exposed to the vapor. Figure 7 details this area showing the discoloration.

Figure 5. Type 316LW tested in deionized water at 90°C.

Figure 6. Type 316LW tested in 20-wt% hydroxide solution at 90°C.

Figure 7. Type 316LW U-bend coupons showing liquid/vapor interface area.

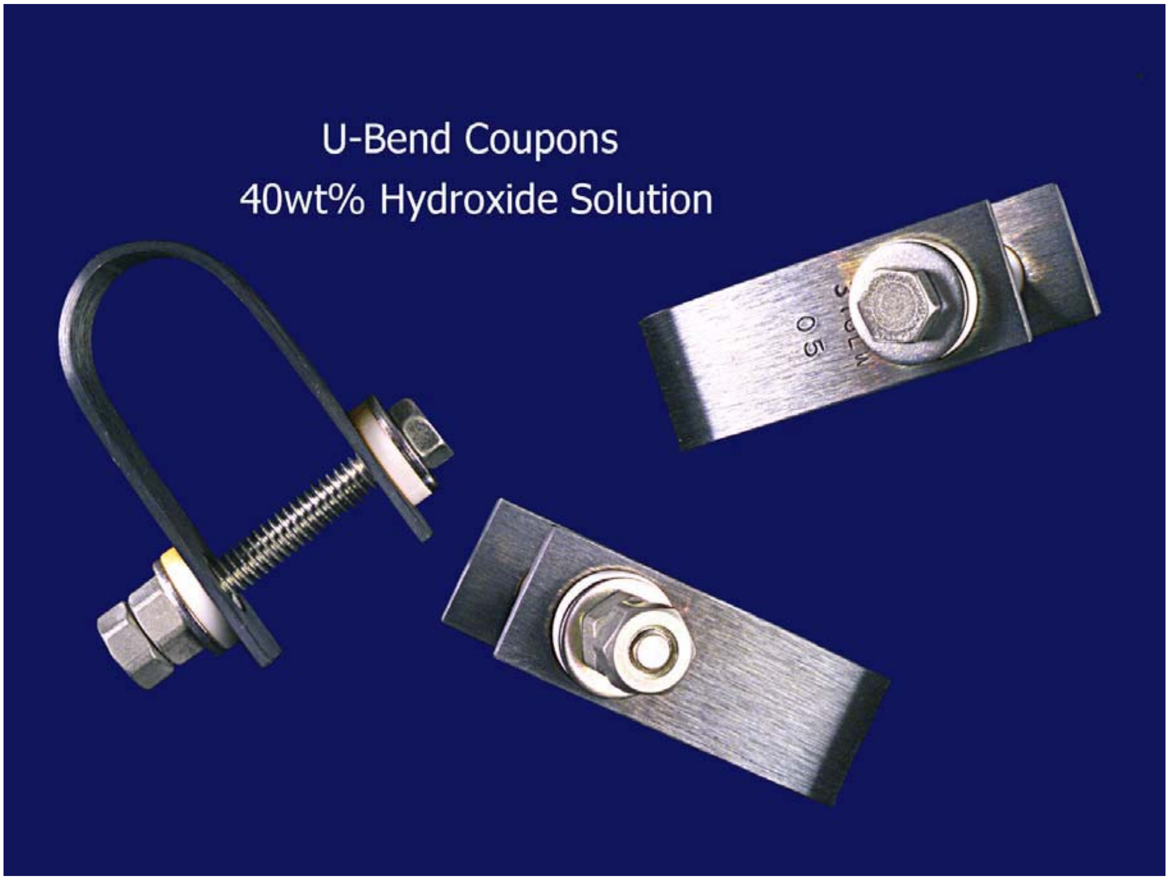

Figure 8. Type 316LW tested in 40-wt% hydroxide solution with halides at 90°C.

Results from the 316LW U-bend tests in the 40-wt% hydroxide solution with halides was similar. After 6 months of exposure, no cracking was identified on the three coupons. Microscopic examination of coupon numbers 5 and 6 revealed openings that also looked like deformation damage caused by the initial bending of the coupon. This damage did not change throughout the test period and is assumed to have occurred during the bending of the coupon. A small weight loss trend indicated a small level of general corrosion was occurring, which correlated to the results of the crevice tests. The solution has turned the coupons a dark brown overall as can be seen in Figure 8. The general corrosion was worse in the vapor space portion of the coupon as opposed to the immersed section in the same fashion as the coupons tested with the 20-wt% solution. Figure 7 also details the interface area of the coupon tested with the 40-wt% hydroxide solution.

The 316LW U-bend tests in the 40-wt% hydroxide solution without halides were immersed for 5 months at 90°C, and no indications of cracking were identified. Discoloration was more pronounced without the iodine and bromine (see Figure 9). However, microscopic examination and weight loss measurements were similar to the tests with halides included in the test solution.

Figure 9. Type 316LW tested in 40-wt% hydroxide solution without halides at 90°C.

Similar results were seen with 316L, unwelded coupons in 40-wt% hydroxide solution with halides at 90°C after 5.5 months; shown in Figure 10. General corrosion was worse in the vapor space portion of the coupon as opposed to the immersed section, as seen in the other U-bend tests. No difference was seen in the results compared to the welded coupons. Heat input from welding can cause a region around the weld that is more susceptible to localized and general corrosion than the bulk material. Weld areas were not preferentially attacked in the U-bend experiments, thus no increased susceptibility to cracking due to welding was indicated.

5.3 Type 316L Slow Strain Rate Tests

Two weld configurations were investigated in the SSRTs: a transverse weld across the gage area and a weld longitudinally down the test coupon. Each weld configuration had a baseline test in deionized water and was then tested with the 20-wt% and 40-wt% hydroxide solutions containing halides. Triplicate test coupons were not used for this test method because of the time duration of each test. Single tests in conjunction with the triplicate crevice and U-bend tests will provide the necessary confidence in the stainless steels resistance to cracking. The time (in hours) to failure of each of the tests is shown in the Table 4.

The results of the SSRTs indicate there is little probability of these solutions causing a stress crack in the Type 316LW stainless steel material. Times to failure of the test solutions deviated less than 5% from the baseline tests. This is within the repeatability of the test equipment. In addition, visual observations under a microscope showed no indications of cracking. The failures appeared to be ductile in all coupons tested. Selected samples were examined with a scanning electron microscope to verify the appearance of a ductile fracture. Brittle fractures typically have no plastic deformation such as necking and side peaks as seen in Figure 11. Chevron (V-shaped) lines are also often seen on the fracture face in a brittle fracture; however, a dimpled surface indicative of ductile failures was found in these tests and is seen in Figure 11.

Figure 10. Type 316L (unwelded) tested in 40-wt% hydroxide solution with halides at 90°C.

Table 4. SSRT results of Type 316LW testing.

Slow Strain Rate Test Results of Type 316L Transverse Welded Coupons	
Test Solution	Time to Failure (hours)
Baseline deionized water	168
20-wt% hydroxide, (w/ B and I)	160
40-wt% hydroxide, (w/ B and I)	160
Slow Strain Rate Test Results of Type 316L Longitudinally Welded Coupons	
Test Solution	Time to Failure (hours)
Baseline deionized water	161
20-wt% hydroxide, (w/ B and I)	156
40-wt% hydroxide, (w/ B and I)	155

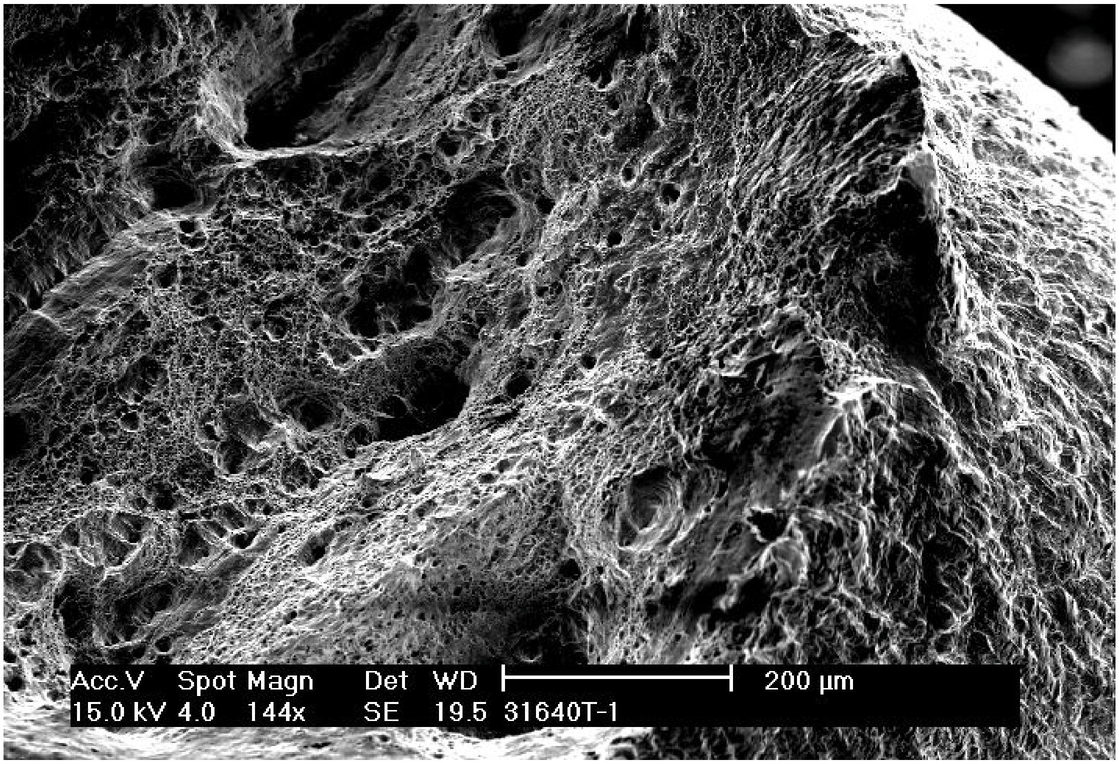

Figure 11. SEM photo of the fracture surface of type 316L, transverse weld, slow strain rate test sample exposed to 40% caustic solution.

5.3.1 Type 316L Conclusions

The combined results of the crevice, U-bend, and SSRT methods indicate that the tested Type 316LW and 316L (unwelded) material most likely will not be susceptible to cracking from potential cesium and rubidium hydroxide solutions. Welding changes the metallurgical structure near the weld, but it had no effect on the SCC susceptibility in these tests. Corrosion rates from those coupons tested with the hydroxide solutions did not significantly differ from the control coupons tested in deionized water. Welded coupons had similar results to the unwelded samples, indicating no increased susceptibility from the heat input. In addition, the corrosion rates from the hydroxide solution without halides did not differ significantly from the hydroxide solution containing the halides, indicating iodine and bromine do not have an effect on the corrosion susceptibility of the Type 316L stainless steel. No visual indications of cracking or pitting were seen from the crevice and U-bend experiments, and no decrease in failure time was found in the SSRTs. In conclusion, the 316L stainless steel standard canisters should not fail prematurely because of the presence of cesium and rubidium.

5.4 Type 304L Experimental Results

5.4.1 Type 304LW Crevice Tests

Results listed in Table 5 indicate that the general corrosion rates for Type 304L stainless steel were typically low, similar to the results with Type 316L. As mentioned in Section 5.1, corrosion rates <2 mpy are preferred by industrial standards. Coupon number 9, which was exposed to the 40-wt% solution without halides, is the exception with a corrosion rate of 2.1 mpy. This higher rate was not repeated with the other two crevice coupons in the same test vessel. Visual examination of the coupon did

Table 5. Type 304LW crevice test corrosion rates.

Coupon ID	Alloy	Solution Tested	Corrosion Rate (mpy)
01	304LW	Deionized water	0.000
02	304LW	Deionized water	0.0008
03	304LW	Deionized water	(-0.008)
	(Disregard (-) rate)	**Average Rate =**	**0.004**
10	304LW	20% OH (w/ B and I)	0.03
11	304LW	20% OH (w/ B and I)	0.02
12	304LW	20% OH (w/ B and I)	0.008
		Average Rate =	**0.02**
04	304LW	40% OH (w/ B and I)	0.05
05	304LW	40% OH (w/ B and I)	0.05
06	304LW	40% OH (w/ B and I)	0.07
		Average Rate =	**0.06**
07	304LW	40% OH (w/o B and I)	0.06
08	304LW	40% OH (w/o B and I)	0.07
09	304LW	40% OH (w/o B and I)	2.1
		Average Rate =	**0.74**

not reveal corrosion attack any worse than seen on the other samples. The final weight was repeated, and a review of weights and dimensions compared to the other coupons was performed. No indication of measurement errors was found. Thus, the higher corrosion rate was included in the average rate. No indications of pitting or cracking were seen in any of the tests. Minor crevice corrosion was seen on the coupons tested in both 40-wt% hydroxide solutions. White light interferometer measurements were taken from these corrosion sites, but the surface roughness did not differ from the other parts of the corrosion coupon. Figures 12 through 15 show the final condition of the coupons from all the test solutions. The color of the coupons tested in deionized water remained unchanged except for a few oxide (rust) spots.

The coupons tested in the hydroxide solutions turned a brown color as a result of the chemical attack. The coupons tested in the 40-wt% solution with halides were darker than the ones tested in the 20-wt% hydroxide solution. The coupons tested in the 40-wt% hydroxide solution without halides were the darkest. As discussed in the Type 316L experimental results, the discoloration is only a few angstroms thick. All coupons from the hydroxide solutions showed a tinted footprint where the crevice washer had been placed, but only minor localized corrosion has occurred on the coupons tested in the 40-wt% hydroxide solutions. All the coupons tested in the hydroxide solutions had the welds etched.

Figure 12. Type 304LW tested in deionized water at 90°C.

Figure 13. Type 304LW tested in 20-wt% hydroxide with halides at 90°C.

Figure 14. Type 304LW tested in 40-wt% hydroxide solution with halides at 90°C.

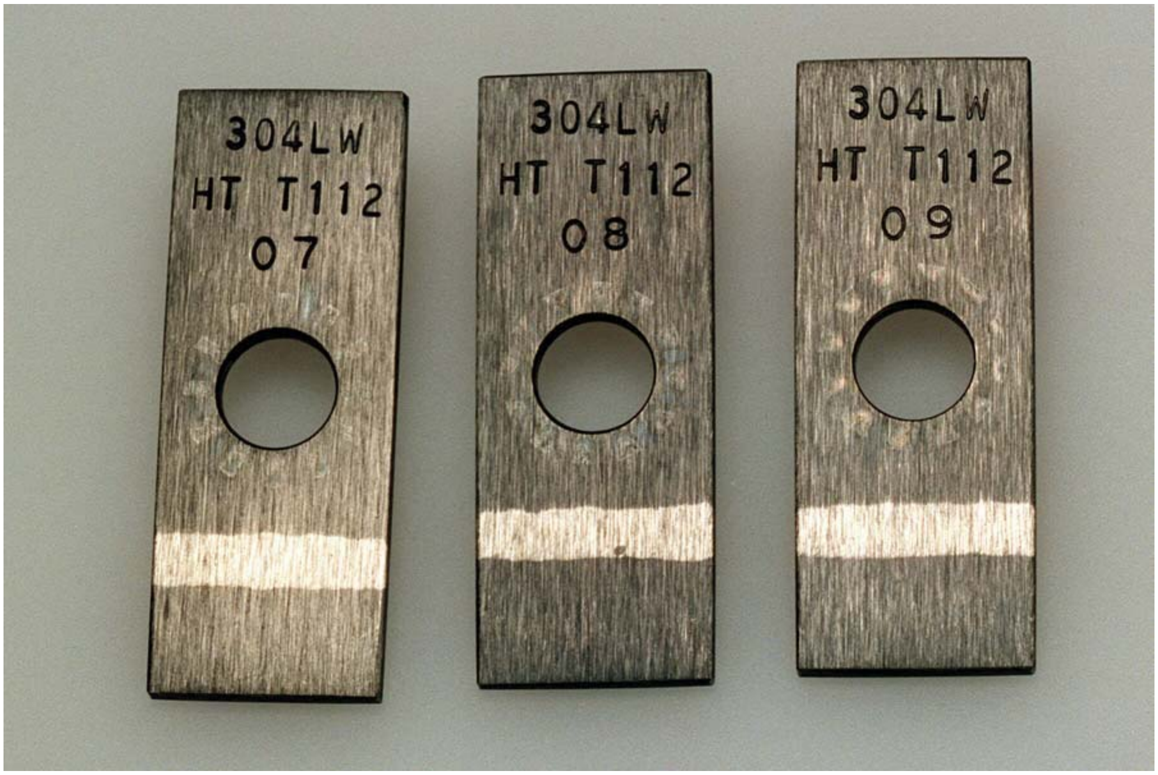

Figure 15. Type 304LW tested in 40-wt% hydroxide solution without halides at 90°C.

5.5 Type 304LW U-Bend Tests

None of the three 304LW U-bend test coupons showed any clear indication of cracking after 6 months in deionized water at 90°C. Weight losses of the U-bend coupons were measured as a general indication of corrosion. A very small weight loss trend (<0.1 g) indicated a small level of general corrosion was occurring, and this correlates to the results of the crevice tests. The coupons did not darken, but some small oxide (rust) spots were visible. Figure 16 shows the post-test appearance of the coupons.

The 304LW U-bend tests in the 20-wt% and 40-wt% hydroxide solutions with halides were immersed for 5 months at 90°C. A small weight loss trend indicated a small level of general corrosion was occurring, but did differ from the losses seen in deionized water. The corrosion appears more prevalent in the vapor space areas as was seen on the other U-bend coupons. Microscopic examination of the triplicate coupons revealed no localized corrosion, such as cracking, was occurring. Figure 17 shows the post-test appearance of the coupons exposed to 20-wt% hydroxide solution. Figure 18 shows the coupons from the 40-wt% hydroxide tests.

Additional experiments were completed to evaluate the effects of halides in the test solution and to assess any increased susceptibility to cracking from the welding operation. Three 304LW U-bend coupons were exposed to 40-wt% hydroxide solution without halides at 90°C for 5 months. Results were very similar to the tests with halides in solution, small weight losses and no visible indications of localized attack such as cracking. Vapor space attack appears to be slightly worse than the areas exposed to solution. Figure 19 is a photograph of the coupons after exposure. Unwelded Type 304L coupons also showed no differences in degradation after 5.5 months in the 40-wt% hydroxide solution with halides at 90°C. Microscopic examination and weight loss measurements were essentially identical between the welded and unwelded coupons. Final conditions are shown in Figure 20.

Figure 16. Type 304LW tested in deionized water at 90°C.

Figure 17. Type 304LW tested in 20-wt% hydroxide solution at 90°C.

Figure 18. Type 304LW tested in 40-wt% hydroxide solution with halides at 90°C.

Figure 19. Type 304LW tested in 40-wt% hydroxide solution without halides at 90°C.

Figure 20. Type 304L (unwelded) tested in 40-wt% hydroxide solution with halides at 90°C.

5.6 Type 304L Slow Strain Rate Tests

Tensile coupons with Type 304L were prepared with the same weld configurations as the Type 316L coupons, a transverse weld across the gage area and a weld longitudinally down the test coupon. Baseline tests with deionized water were performed first with both weld configurations. One longitudinal coupon and one transverse welded coupon were tested with the 20-wt% and 40-wt% hydroxide solutions containing halides. The time (in hours) to failure from each test is shown in Table 6.

Results from the SSRTs indicate Type 304LW stainless steel will probably not fail by SCC in cesium/rubidium hydroxide solutions. All but one of the times to failure deviated less than 5% from the baseline tests, which is within the repeatability of the test equipment. Although the transversely welded 304LW coupon in 40-wt% hydroxide solution deviated 7.9%, visual inspection of the sample found no indications of cracking. In addition, visual observations under a microscope of all coupons and scanning electron microscopy of selected samples revealed ductile fractures. Figure 21 shows the dimpled surface of the fracture face typical of a ductile failure.

5.6.1 Type 304L Conclusions

Based on the results of the crevice, U-bend, and SSRT methods, the potential for Type 304L stainless steel to fail by SSC in cesium and rubidium hydroxide solutions is minimal. Corrosion rates were low and did not differ significantly from the control in deionized water, and the weight losses from the U-bend tests were small. Microscopic examinations found few indications of cracking or pitting, though some degradation effects were seen. Most of the slow strain rate data indicated no decrease in ductility or failure rates. One test (40-wt% hydroxide with the transverse weld) had a slightly low time to failure measurement. The presence of halides did not alter the degradation rates or increase the susceptibility of cracking. Nor did heat input from welding increase localized or preferential attack. Although a few results indicated the risk of SCC with Type 304L stainless steel is slightly greater than with Type 316L, failure because of the presence of cesium and rubidium hydroxide is not expected.

Table 6. SSRT results of Type 304LW testing.

Slow Strain Rate Test Results of Type 304LW Transverse Welded Coupons

Test Solution	Time to Failure (hours)
Baseline deionized water	203
20-wt% hydroxide, (w/ B and I)	194
40-wt% hydroxide, (w/ B and I)	187

Slow Strain Rate Test Results of Type 304LW Longitudinally Welded Coupons

Test Solution	Time to Failure (hours)
Baseline deionized water	187
20-wt% hydroxide, (w/ B and I)	184
40-wt% hydroxide, (w/ B and I)	195

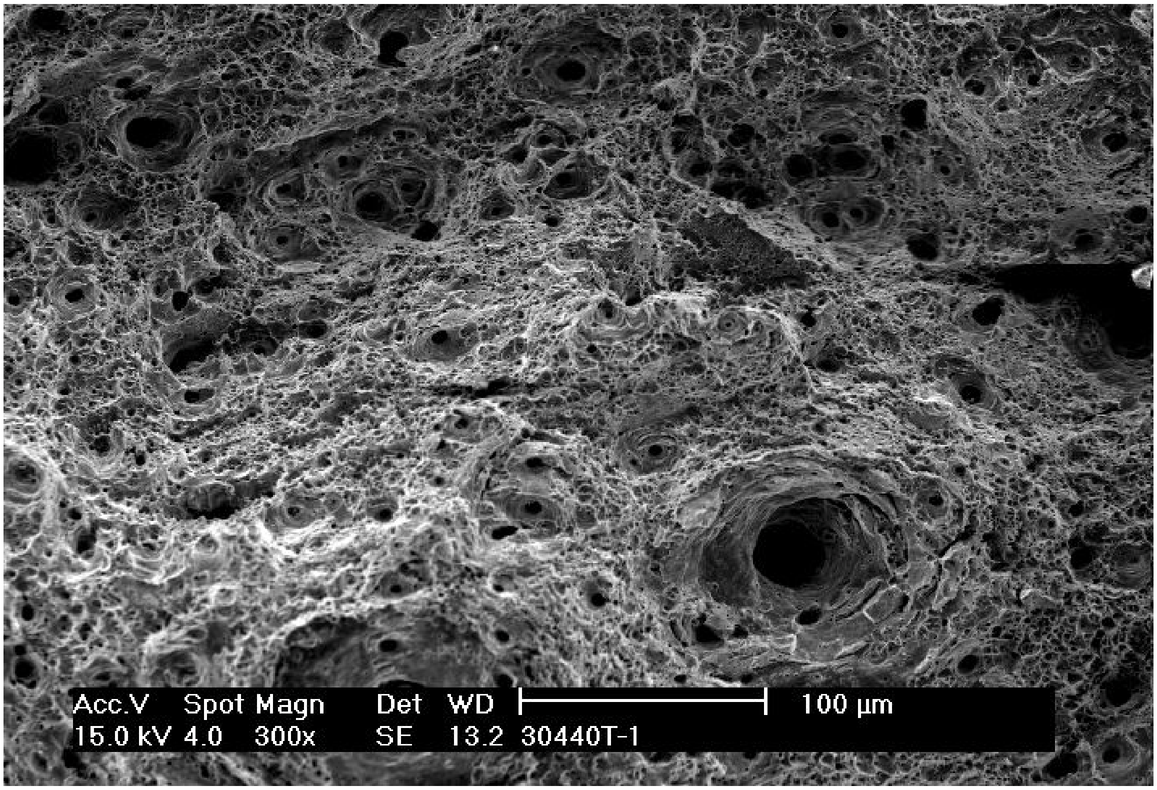

Figure 21. SEM photo of type 304L, transverse weld, fracture surface after exposure to 40% caustic solution in a slow strain rate test.

6. CONCLUSIONS

A sensitivity study on the possible effects of SNF degrading while in storage up to 90 years concluded that liquid cesium and rubidium could pose a canister degradation problem. A review of two failure mechanisms from these elements was performed under this task. Some liquid metals have the potential to cause LME of selected solid metals when they are in intimate contact. A review of the literature indicated that austenitic stainless steels would not be susceptible to liquid cesium or rubidium. However, both elements could react with any water present in the container to form hydroxides. A survey of available research showed that a stress cracking concern may exist for the stainless steel in the presence of caustics.

A research task was initiated to evaluate the susceptibility of Types 304L and 316L stainless steels to SCC by cesium/rubidium hydroxide. Cracking potential can be estimated using a wide variety of test methods. Three were selected for this project (crevice, U-bend, and slow strain rate). Triplicate tests were also conducted, except in the SSRTs, to evaluate for reproducibility. Two solution chemistries, two temperatures, and two material types were evaluated in the experiments.

No indications of accelerated general corrosion or localized corrosion (including cracking) were found in the crevice or U-bend tests with Type 316L stainless steel. Likewise, tensile failure times in the hydroxide solutions did not vary from the deionized water tests more than the equipment variability. Microscopic examination of the coupons indicated a ductile fracture. Some Type 304L coupons showed possible negative effects. Slight crevice attack was seen; one coupon had a corrosion rate above 2 mpy (though this was likely a measurement error), and one tensile specimen had a failure time outside the equipment variability. Discoloration was seen to some degree on all coupons but was very thin, on the order of angstroms. Unwelded coupons were tested under a few selected conditions, but no differences were found in the degradation compared to welded samples. The effects of halides, iodine and bromine, were also assessed in the crevice and U-bend tests. Though they may provide some measure of inhibition to attack, the effect is not significant.

In conclusion, neither the proposed SNF standard canister constructed of Type 316L stainless steel nor the MCO made with Type 304L stainless steel is expected to be susceptible to the presence of cesium and rubidium from the fuel. LME will not be a concern because austenitic stainless steels are not susceptible to those two elements. The metals should also be immune to SCC from cesium/rubidium hydroxide based on the experiments performed in this project. However, Type 304L appears to be slightly more susceptible to localized corrosion in this environment than Type 316L stainless steel.

7. REFERENCES

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